AD-A039 516 CALIFORNIA UNIV SAN DIEGO LA JOLLA DEPT OF CHEMISTRY F/G 7/3
ELECTRICAL AND PHOTOLUMINESCENT PROPERTIES OF SOME SUBSTITUTED --ETC(U)
JAN 75 G N SCHRAUZER, H PRAKASH N00014-69-0200-6035

UNCLASSIFIED TR-10 NL

| OF |

AD
A039516

END

DATE
FILMED
6-77

OFFICE OF NAVAL RESEARCH

15 Contract No. N00014-69-A-0200-6035 new

Task No. NR 053-529

9 Technical Report No. 10

14 TR-10

6 Electrical and Photoluminescent Properties of Some Substituted Copper(I) Thiophenolates

by

10 G.N. Schrauzer ~~and~~ H. Prakash

Department of Chemistry
University of California
San Diego, California 92037

January 8, 1975

11 8 Jan 75

12 7p.

ELECTRICAL AND PHOTOLUMINESCENT PROPERTIES OF SOME SUBSTITUTED COPPER(I) THIOPHENOLATES

INTRODUCTION:

In a recent paper, we reported the electrical and photoluminescent properties of copper(I)thiophenolate.[1] The complex, for which a linear S-bridged polymeric structure was postulated, had an electrical resistivity of 5.1×10^4 ohm·cm at room temperature with a relatively low thermal activation energy for conduction (E_a = 0.11 ev). When excited by 3650 Å ultraviolet light at room temperature, it appeared pink-red. Preliminary spectral work indicates that the photoluminescent behavior may be intrinsic and not caused by any impurity or photochemical reaction. Following the original research proposal, we have now synthesized a number of copper(I) complexes of substituted thiophenols to investigate the substituent(inductive, mesomeric and steric) effects on the electrical and photoluminescent properties.

EXPERIMENTAL:

<u>Synthesis of the Complexes</u>. Three general methods were employed for the synthesis of the copper(I) thiophenolates reported here.

<u>Method A</u>. Freshly prepared CuCl with a slight excess of the corresponding thiophenol in absolute ethanol was refluxed for several hours under argon. The complex was filtered, thoroughly washed with boiling ethanol and benzene and dried <u>in vacuo</u> at 150°C. Prepared by this method were the complexes in entries 1, 4, 6, 7, 12 and 13 in Table 1.

<u>Method B</u>. An ethanolic solution of $CuCl_2$ was gradually added to an ethanolic solution of the corresponding thiophenol under argon, using generally a 100%

excess of the thiophenol. The reaction mixture was refluxed for several hours. The insoluble complex was filtered, washed thoroughly with boiling ethanol and benzene and dried in vacuo at 150°C. Prepared by this method were the complexes in entries 2, 3, 5 and 8-10 in Table 1.

Method C. The complex in entry 11 was prepared by first refluxing 2.0 ml of benzaldehyde, 2.5 g of 4-aminothiophenol and 2.0 ml of triethyl amine in 150 ml 95% ethanol for two hours. Freshly prepared 1.5 g CuCl was then added to the reaction mixture. After refluxing over night under argon, the yellow-green solid complex was filtered, thoroughly washed with boiling ethanol and benzene and dried in vacuo at 150°C. Yield: 3.8 g; theory requires for $CuS\text{-}C_6H_4\text{-}N{=}CH\text{-}C_6H_5$: 4.2 g based upon CuCl.

The physical, electrical and photoluminescent properties of the complexes prepared in this study are given in Table 1.

Table I

PHYSICAL, ELECTRICAL AND PHOTOLUMINESCENT PROPERTIES OF SOME SUBSTITUTED COPPER(I) THIOPHENOLATES

Entry	Complex	Color	Dec. Temp. (°C)	ρ_{25} (ohm·cm)	Color after excitation by 3650Å
1	Copper(I)thiophenolate, C_6H_5SCu	Yellow	>280	5.1×10^4	Pink-red
2	Copper(I)pentafluorothiophenolate, C_6F_5SCu	Yellow	>240	9.90×10^7	Orange
3	Copper(I)pentachlorothiophenolate, C_6Cl_5SCu	Light brown	>230[a]	Not cond.	Dark purple
4	Copper(I)-4-bromothiophenolate, $C_6H_4(Br)SCu$	Yellow	>260	2.3×10^8	Orange
5	Copper(I)-3-methylthiophenolate, $C_6H_4(CH_3)SCu$	Yellow	250-55[a]	3.6×10^4	Pink-red
6	Copper(I)-4-t-butyl-2-methylthiophenolate, $C_6H_3(t\text{-}C_4H_9)(CH_3)SCu$	Yellow	240-45[a]	3.6×10^7	Red
7	Copper(I)-4-bromo-3-methylthiophenolate, $C_6H_3(Br)(CH_3)SCu$	Yellow	240[a]	$\sim 10^8$	Orange
8	Copper(I)-2-isopropylthiophenolate, $C_6H_4(C_3H_7)SCu$	Yellow	245-48[a]	1.7×10^8	Red
9	Copper(I)-4-methylthiophenolate, $C_6H_4(CH_3)SCu$	Yellow	257-61[a]	4.5×10^5	Red
10	Copper(I)-2,3-dichlorothiophenolate, $C_6H_3Cl_2SCu$	Yellow-brown	>270	1.0×10^9	Red
11	$CuS\text{-}C_6H_4\text{-}N{=}CH\text{-}C_6H_5$	Yellow-green	>220-40	Not cond.	Purple
12	$C_4H_3N_2SCu$ (copper complex of 2-mercaptopyrimidine)	Yellow	Stable to 340	Not cond.	Purple
13	$C_3N_3S_3Cu_3$ (copper complex of trithiocyanuric acid)	Red	Stable to 340	Not cond.	Red

RESULTS AND DISCUSSION:

The results indicate that the substituents on the phenyl ring can cause an increase or decrease in the electrical conductivity of the copper thiophenolate, C_6H_5SCu by several orders of magnitude depending on the nature and position of substitution. In general, substitution at positions ortho or para to the mercapto functional group results in a decrease of the electrical conductivity regardless of the nature of the substituents. The methyl substituent at the meta position, however, has the effect of increasing the electrical conductivity of the parent copper thiophenolate by about 30%. We, however, refrain to generalize this later effect since the examples of meta-substituted thiophenolates are too few to allow any meaningful correlations with the conductivity. Several trends can be seen from the data presented here.

1) Halogen substituents decrease the conductivity by roughly 10^4 orders of magnitude or more. Fluoro-substituted complexes are better conductors than either the bromo- or chloro-substituted complexes. The chloro-substituted complexes become virtually insulators.

2) Further substitution of the bromo-substituted complex at the meta position by the methyl group results in a slight increase of the conductivity of the parent complex. This increase is again a reflection of the tendency of the methyl group at the meta position to promote electron transport.

3) Not only that the electrical conduction is affected by the inductive or the mesomeric effects but that the steric requirements of the substituents may also play an important role in determining the electrical conductivity, is nicely illustrated by the alkyl substitution at the ortho and para positions. Although

para-substitution by methyl group decreases the conductivity by only 9 orders of magnitude(entry 9), an enormous decrease results in the electrical conductivity when isopropyl group is substituted at the ortho position(entry 8). Therefore, the effects of ortho substitution by the alkyl groups on the electrical conductivity are far more pronounced than the para substitution. It is interesting to note that the conductivity of the copper(I)-4-t-butyl-2-methylthiophenolate is slightly higher than copper(I)-2-isopropylthiophenolate despite substitution at the ortho position in both complexes. It is likely that the less bulky methyl group in ortho position decreases the conductivity to a lesser extent than the more bulky isopropyl group. Such a conclusion is to be regarded with caution as the conductivity of the copper(I)-2-methylthiophenolate has not been measured for a valid comparison. Nevertheless, such steric effects will be particularly important in influencing the electrical conduction if the conduction mechanism would involve intermolecular transfer of electrons via Cu-Cu bonds. The bulkier substituents in the proximity of the mercapto functional group would tend to prevent a close approach of the metal atoms to form strong metal-metal bonds as a result of stacking of the linear polymeric chains in the solid state.

All complexes reported here exhibit photoluminescence in the visible region when excited by 3650 Å ultraviolet light. The energy and the efficiency of the emitted radiation which covers almost the entire visible region depends again on the nature of the substitution. Whereas unsubstituted and alkyl-substituted copper(I) complexes emit in the red region, the emission shifts to the shorter wavelengths when halogens are the substituents. Thus, although bromo- or fluoro- substituted complexes emit in the orange region, the chloro-substituted complexes appear purple after excitation. In general, bromo- and alkyl-substituted copper thiophenolates are more efficient emitters of energy.

The details of the electrical and photoluminescent properties are presently under investigation.

SUMMARY:

Substituted copper(I) thiophenolates which combine interesting electrical and photoluminescent properties have been synthesized. These materials in which the electrical and photoluminescent properties can be controlled over a wide range by a judicial variation of the substituents in the phenyl ring, can find potential uses in devices in which an irreversible change of electrical conductivity on illumination is desired.

REFERENCES:

1. "The Synthesis and Electrical Properties of Transition Metal Mercaptides of 1,4-Dimercaptobenzene", G. N. Schrauzer and H. Prakash, to be published in Inorganic Chemistry, April, 1975.